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<p>(54) Title: COMPOSITION AND PROCESS FOR TREATING A METAL SURFACE</p> <p>(57) Abstract</p> <p>A process for treating a zinciferous surface that affords an excellent resistance to black tarnishing and an excellent resistance to white rust comprises treating the zinciferous surface with an acidic aqueous solution with a pH of 1.5 to 4.5 that contains at least one type of heavy metal ions selected from iron, cobalt, and nickel and also contains zinc ions and/or aluminum ions, rinsing with water the surface thus treated, and subjecting the thus rinsed surface to a dry-in-place chromate treatment.</p>		

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Description**COMPOSITION AND PROCESS FOR TREATING A METAL SURFACE****FIELD OF THE INVENTION**

The present invention relates to a process for treating a metal surface, preferably a surface that is at least 50 % by weight zinc, more preferably a surface of hot-dip zinciferous-coated steel sheet, that imparts thereto an excellent resistance to black tarnishing and to white rust. Further description below will be primarily in terms of treatment of hot-dip galvanized steel sheet, but it should be understood that the process applies to any other zinciferous surface and more generally to any sufficiently active metallic surface that is susceptible to tarnishing, other discoloration, or corrosion.

DESCRIPTION OF RELATED ART

The sacrificial corrosion protection of iron and steel is most effectively and efficiently carried out using zinc coating, with the result that ten percent of Japan's annual raw steel production of one hundred million tons, or ten million tons, takes the form of zinc-coated steel sheet. This product is widely used, *inter alia*, as a construction material, in automobiles, and in household electrical appliances. Sacrificial corrosion protection by zinc is based on the formation of a cell where the two metals (zinc and iron or steel) are in contact. The zinc, as the baser metal, functions as the anode and the iron is made the cathode. This prevents the anodic dissolution that would occur due to local cell formation in the case of iron by itself and thereby prevents corrosion of the iron or steel. Given this mechanism, the rust-preventive function ends when zinc is no longer present in contact with the iron or steel, and the zinc layer itself must therefore be protected from corrosion in order for it to continue its activity long-term. Chromate treatment of zinciferous surfaces has been generally practiced as a countermeasure to zinc corrosion.

Unfortunately, this corrosion-preventing chromate treatment is associated with various problems: While the chromate treatment of hot-dip zinciferous-coated steel sheet does result in a substantial inhibition of white rusting, it produces a black tarnish during storage or transport that impairs the appearance. It has been observed that black tarnish is more readily produced on stock that has been skin-pass rolled after hot-dip zinc coating, on hot-dip zinciferous-coated steel sheet produced using a lead-containing coating bath, and on steel sheet hot-dip coated with zinc/aluminum alloy containing several percent of aluminum. A characteristic feature of this black tarnishing is that a grayish-black color occurs in particular in regions of a specific crystal direction in the spangle on the coated surface. Minimizing spangle using well-known methods is

therefore effective to some degree in dealing with black tarnishing. Lead particles are also present within spangle that produces black tarnishing, and these lead particles function as active sites that accelerate black tarnishing. As is known, black tarnishing can be inhibited when the lead in the coating bath is reduced to very low levels (≤ 0.01 %) in order to counter black tarnishing. At the same time, however, many users desire the presence of spangle on hot-dip zinciferous-coated steel sheet, and as a consequence the addition of lead to the coating bath cannot be avoided. Another problem occurs when a chromating treatment is carried out on steel sheet that has been hot-dip coated with zinc/aluminum alloy. This material has an excellent corrosion resistance and as a result has recently frequently been used directly in an unpainted condition. However, since the coating layer in this case contains a high concentration of aluminum, the local cell activity originating from the zinc and aluminum causes black tarnishing to be substantially more accelerated — and thus causes the commercial value to be correspondingly reduced — than in the case of ordinary hot-dip zinc-coated steel sheet.

At present, flash treatments are viewed as an effective means for solving the problems described above, that is, black tarnishing after a chromate treatment. Flash treatment, as known, for example, from Japanese Published Application (Kokoku or Examined) Number Hei 3-49982 (49,982/1991), involves treatment, for example, with an aqueous solution containing Ni^{2+} and/or Co^{2+} , in order to chemically deposit trace amounts of metal. In order to prevent black tarnishing, Japanese Published Application (Kokoku or Examined) Number Hei 3-49982 essentially teaches a pre-chromating flash treatment of the surface of hot-dip zinc- or zinciferous-coated steel sheet with an aqueous solution that contains either or both of the metal ions Ni^{2+} and Co^{2+} and has a pH from 1 to 4 or from 11 to 13. This treatment results in the deposition of the metal ions as the metal or oxide and is followed by a water rinse and then formation of a chromate coating.

Another flash treatment process is taught in, for example, Japanese Published Application (Kokoku or Examined) Numbers Hei 3-52546 (52,546/1991) and Hei 5-2741 (2,741/1993). In this treatment methodology, a flash treatment is carried out while selectively removing the Al and Al oxide on the surface of hot-dip zinciferous-coated steel sheet by treatment with an alkaline aqueous solution containing Fe ions and trace amounts of Ni ions and having a pH from 9 to 14.

While the flash treatment taught in Japanese Published Application (Kokoku or Examined) Number Hei 3-49982 does inhibit black tarnishing when executed prior to chromating, this flash treatment also has a pronounced tendency to deposit excessively

large amounts of metal. The add-on of these different metals on the surface of the zinc coating has the adverse result of readily causing the appearance of white rust.

In the case of Japanese Published Application (Kokoku or Examined) Number Hei 3-52546, aluminate ions and zincate ions are present in order to prevent excessive deposition of Fe, etc., but due to the use of an alkaline solution the amount of dissolving aluminum and zinc present dissolved as the ions is very small. As a result this treatment is accompanied by the generation of large amounts of a sludge that is mainly zinc hydroxide and aluminum hydroxide. Not only does this sludge impair line operations by clogging the pipework and nozzles, but metal ions such as those of Fe also simultaneously coprecipitate as sludge, which prevents the generation of desirable add-ons and leads to an unstable performance with regard to the resistance to black tarnishing.

OBJECT OF THE INVENTION

This invention seeks to provide a process for treating the surface of metal, particularly hot-dip zinciferous-coated steel sheet, that accomplishes at least one, and most preferably all, of the following objectives: (i) simultaneously achieving resistance to black tarnishing and white rust; (ii) avoiding the coprecipitation of heavy metal ions in sludge — even as the concentration of dissolving zinc and aluminum ions increases during treatment — and thereby providing a stable performance over an extended period of time from the initial period following bath make-up; and (iii) eliminating the necessity for a sludge removal operation.

BRIEF SUMMARY OF THE INVENTION

It has been found that (i) addition of zinc ions and/or aluminum ions to an acidic substitutional-plating bath restrains the amount of deposition of Fe, Co, and/or Ni, which are collectively referred to hereinafter as "heavy metals", in the initial period following bath make-up; (ii) the presence of both fluoride (as typified by hydrogen fluoride) and phosphoric acid in the subject acidic aqueous solution improves its dissolution-promoting activity with respect to the surface of zinciferous-coated steel sheet and particularly the oxide coating thereon; and (iii) restricting the amount of the component contributing to etching and maintaining the pH between 1.5 and 4.5 stably produced hot-dip zinciferous-coated steel sheet that is thoroughly inhibited against black tarnishing and white rusting.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The present invention provides a process comprising, preferably consisting essentially of, or more preferably consisting of, the following operations:

- (1) treating a metallic surface, preferably a surface of hot-dip zinciferous-coated steel sheet with an acidic aqueous solution having a pH from 1.5 to 4.5 and containing at least one type of heavy metal ions selected from the group

- consisting of iron, cobalt, and nickel along with zinc ions and/or aluminum ions;
- (II) rinsing the surface thus treated with water; and thereafter
 - (III) subjecting the rinsed surface to a dry-in-place chromate treatment.

The above-referenced acidic aqueous solution with a pH from 1.5 to 4.5 preferably, in addition to water, comprises, more preferably consists essentially of, or still more preferably consists of: from 1 to 200 grams of sulfate ions per liter of solution, the concentration unit of grams of a material per liter of solution being hereinafter usually abbreviated as "g/L"; from 0.3 to 3 g/L of phosphate ions; from 0.3 to 3 g/L of fluoride ions; from 1 to 15 g/L of organic acid; from 0.05 to 5 g/L of heavy metal ions; and from 1 to 50 g/L of zinc ions and/or aluminum ions.

The hot-dip zinciferous-coated steel sheet treated according to the present invention is not limited and can be exemplified by the usual steel sheet hot dip-coated with Zn containing from 0.1 to 0.3 % Al, steel sheet hot dip-coated with Zn containing the same amount of Al and from 0.05 to 0.3 % Pb, and steel sheet hot dip-coated with zinc/aluminum alloy containing from 0.3 to 6.0 % Al and trace amounts of La, Ce, Mg, etc.

Zinc ions and/or aluminum ions are present in the acidic aqueous solution used for treatment, preferably initially at a total concentration from 1.0 to 50 g/L, or more preferably from 3.0 to 35 g/L. The zinc ions and/or aluminum ions are desirably added as the sulfate, phosphate, nitrate, carbonate, oxide, hydroxide, or organic acid salt. The long-term use of chlorides can lead to an accumulation of chloride ions and therefore to an increased risk of corrosion of the coating equipment. The presence of these ions at less than 1 g/L does little or nothing to inhibit excess deposition of the iron, cobalt, and nickel heavy metal ions and thus causes a decline in the resistance to white rusting. The effect from zinc ions and/or aluminum ions is saturated at above 50 g/L, and additions in excess of this level therefore achieve nothing more than a substantial economic loss.

The sulfate ions preferably are supplied from sulfuric acid, and, because the sulfate ions are believed to capture or scavenge the zinc ions and aluminum ions dissolving from the hot-dip zinciferous-coated steel sheet, more sulfate preferably will be added as the zinc and/or aluminum ions continue to dissolve, most preferably in an amount such that the pH value of the acidic aqueous treatment solution does not rise by more than, with increasing preference in the order given, 0.50, 0.40, 0.30, 0.20, or 0.10 pH unit over its initial value before the acidic aqueous treatment solution began to be used in the process, and independently preferably does not fall by more than, with increasing preference in the order given, 1.1, 0.9, or 0.7 pH unit below said initial value. The optimum level of sulfate ions is therefore determined by the amount of etching and the

amount of coating bath removed, but initial concentrations generally preferably are in the range from 1 to 200 g/L, or more preferably from 10 to 65 g/L. Less than 1 g/L is usually inadequate for scavenging the dissolving zinc ions and aluminum ions. At more than 200 g/L, the ability to rapidly remove aluminum is reduced and large amounts of sulfate ions will remain on the coated surface in the absence of a thorough ensuing water rinse, resulting in a decline in the resistance to white rust.

Orthophosphoric acid is preferably used to supply the phosphate ions, and the acidic aqueous solution preferably contains from 0.3 to 3, or more preferably from 0.7 to 2.5, g/L of phosphate ions. The use of less than 0.3 g/L has a negative impact on the aluminum removal activity at increased levels of zinc and aluminum ions and also results in a reduced pH-buffering capacity when little organic acid is present. This often fails to avoid sharp increases in the pH and alterations in the component balance. The use of more than 3 g/L leads to an increased amount of etching, which through the correspondingly facilitated deposition of the iron, cobalt, and nickel heavy metal ions leads to a reduced resistance to white rusting.

The source of the fluoride ions preferably is at least one selection from hydrofluoric acid and fluorosilicic acid. The acidic aqueous solution should contain from 0.3 to 3, or more preferably from 0.5 to 2.5, g/L of fluoride ions. The use of less than 0.3 g/L has a negative effect on the ability to rapidly scavenge aluminum ions at increased levels of zinc and aluminum ions. The use of more than 3 g/L leads to an increased amount of etching, which through the correspondingly facilitated deposition of the iron, cobalt, and nickel heavy metal ions leads to a reduced resistance to white rusting. The use of more than 3 g/L also facilitates corrosion of the equipment, even stainless steel equipment, when a low pH range is maintained.

The organic acid is supplied by at least one selection from the group consisting of glycolic acid, lactic acid, malic acid, tartaric acid, citric acid, gluconic acid, and ascorbic acid. The organic acid content preferably is from 1 to 15 g/L. The use of less than 1 g/L of organic acid results in a weak pH-buffering capacity, which in the case of large amounts of sulfuric acid replenishment will permit the pH to drop below its preferred lower limit and hence runs the risk of equipment corrosion. No additional benefits are obtained for additions in excess of 15 g/L, which makes such additions uneconomical.

Wherever above acids are specified as preferred sources, it is to be understood that salts of the specified acids can be used as alternative sources, provided that some other acid is used to assure that the aqueous solution as a whole has the required pH value. Ordinarily, however, the acids are preferred as the sources over their salts, because using the acids ordinarily is the most economical approach to obtain all of the

preferred characteristics of the aqueous solution. Also, wherever herein ionic solutes are specified as preferred within a certain concentration range, the entire stoichiometric content of the ionic solutes contained within the compound in which they are supplied to the solution is to be assumed to be supplied to the solution for purposes of determining whether solutions conform to the stated preferred concentrations for ionic constituents, irrespective of the actual degree of ionization that may prevail in the aqueous solutions.

In order to increase the amount of etching that can be obtained in a short period of time, the acidic aqueous solution according to the present invention must contain at least one type of heavy metal ions selected from iron, cobalt, and nickel. These ions function to support or assist etching, which is the initial reaction in substitutional plating. These heavy metal ions are desirably supplied by the sulfate, phosphate, nitrate, carbonate, oxide, hydroxide, or organic acid salt of the heavy metal. The chloride should be avoided because accumulation of the chloride ions during long-term operations raises the risk of equipment corrosion.

The concentration of heavy metal ions in the acidic aqueous solution according to the present invention should be from 0.05 to 5 g/L and is preferably from 0.1 to 1.5 g/L, in each case measured as its stoichiometric equivalent as the metal. The desired etching activity usually cannot be obtained at less than 0.05 g/L. A content in excess of 5 g/L has a strong tendency to cause an excessive metal deposition and thus to make the process uncontrollable.

With regard to the activity of these three heavy metals in acidic aqueous solution, the potentials of cobalt and nickel are about the same, but they have a fairly large potential difference from iron. The simultaneous presence of two metals exhibiting a potential difference, i.e., the iron ions/cobalt ions combination or the iron ions/nickel ions combination, activates the substitutional plating reaction and is effective for preventing the decline in reactivity that occurs when large amounts of zinc ions and/or aluminum ions have been admixed. In addition, iron compounds are less expensive than cobalt and nickel compounds and thus offer substantial cost benefits for the high-consumption lines of iron and steel producers.

The acidic aqueous solution according to the present invention with the above-described component composition must have a pH in the range from 1.5 to 4.5. A low pH can be adjusted upward by the addition of zinc or aluminum oxide or ammonia. The pH is restricted to the 1.5 to 4.5 range for the following reasons: A pH below 1.5 is indicative of the presence of excessive amounts of inorganic acid, which has the direct effect of increasing the amount of etching. A too low pH also raises the risk of equipment corrosion. At the other extreme, sludge will tend to be produced in the treatment bath. Use

of a sulfuric acid-based replenisher will normally prevent the pH from rising above 4.5.

Treatment of the hot-dip zinciferous-coated steel sheet can be effected by contacting the sheet surface with the above-described acidic aqueous solution by spraying or dipping followed by a water rinse and then drying.

5 A satisfactory temperature for the acidic aqueous solution is from room temperature (i.e., 18 - 23 °C) to 80 °C, or more preferably from 47 to 63 °C, while a satisfactory treatment time is not more than 15 seconds, or preferably is from 2.5 to 10 seconds. The deposition of less than 5, or more preferably less than 3.5, milligrams of heavy metal per square meter of substrate surface treated will provide a satisfactory inhibition of black
10 tarnishing without lowering the resistance to white rust. (The units of milligrams and grams of a coating material or constituent thereof per square meter of substrate surface coated are hereinafter usually abbreviated as "mg/m²" and "g/m²" respectively.) A lower limit for the amount of deposition is not specified for the following reason: even at a heavy metal deposition of 0 mg/m² an inhibition of black tarnishing will still be obtained
15 as long as the treatment bath composition is maintained within the range given for the present invention as described hereinabove. The deposition of 5 mg/m² or more is undesirable because such levels lead to a reduction in the resistance to white rust.

The water rinse is desirably carried out so as to provide a dilution of at least 500-fold in order to avoid carrying over the components of the acidic aqueous solution into
20 the ensuing dry-in-place chromate treatment bath.

Drying should be carried out to a point that results in elimination of the moisture, and a sheet temperature in the range from 50 to 100, more preferably at least 60, °C is generally preferred.

After the surface of the hot-dip zinciferous-coated steel sheet has been treated
25 with the above-described acidic aqueous solution, the sheet is subjected to a dry-in-place chromate treatment and is then dried without the execution of a water rinse. The conditions employed in this dry-in-place chromate treatment are not narrowly limited, and it will be sufficient simply to use a known chromate treatment technology to provide a chromium add-on from 5 to 100, preferably from 10 to 75, or more preferably from 20 to
30 30, mg/m².

This invention will be illustrated in greater detail through working examples. These examples are provided simply in order to explain the present invention and in no way limit the present invention.

Examples 1 to 3 and Comparative Examples 1 to 4 — General Conditions

35 1. The substrate test sheets were hot-dip zinc-coated steel sheets (Al : 0.2 %, Pb : 0.15 %, coating add-on = 90 g/m², regular spangle stock, sheet thickness = 0.8

millimeter, hereinafter usually abbreviated as "mm"), uncoiled.

2. The dry-in-place chromate treatment utilized an aqueous solution containing 4 % of Cr(VI) and 1 % of Cr³⁺, which was applied by roll coating so as to provide a chromium add-on of 25 mg/m². Application was followed by drying in a 200 °C convection drying oven to a maximum attained sheet temperature of 80 °C.

3. Accelerated testing of the resistance to black tarnishing was performed as follows: A plurality of 70 × 150 mm test coupons were cut from the particular sample test sheet. Pairs of test coupons with their test surfaces facing each other were stacked and wrapped in vinyl-coated paper. Bolts were snugged down at the four corners of the stack, and a load of 70 kilograms force • centimeter was applied using a torque wrench. The stacked and bolted assembly was then allowed to stand in a humidity tester at 50 °C and 98 % relative humidity for 240 hours. Subsequent to this the occurrence of black tarnishing on the stacked surfaces was visually evaluated and scored on the following scale:

+++	:	no black tarnishing
++	:	very slight graying
+	:	some grayish-black discoloration was produced
x	:	substantial grayish-blackening to blackening

4. Accelerated testing of the resistance to white rusting was performed as follows: A 70 × 150 mm test coupon was cut from the particular sample test sheet and submitted to salt-spray testing as specified in Japanese Industrial Standard Z-2371 for 96 hours. The area of white rust production was then visually evaluated and scored on the following scale.

+++	:	no white rust
++	:	area of white rust production < 5 %
+	:	area of white rust production from 5 % (inclusive) to < 25 %
x	:	area of white rust production 25 % or greater.

5. The source compounds for the following ingredients reported in the compositions in the tables below were as follows: FeSO₄•7H₂O for Fe, CoSO₄•7H₂O for Co, NiSO₄•6H₂O for Ni, 75 % orthophosphoric acid for PO₄³⁻, 40 % fluorosilicic acid for F, ZnSO₄•7H₂O for Zn, and non-stoichiometrically hydrated aluminum sulfate for Al. Sulfuric acid and ammonia were used to adjust the pH of the treatment bath.

Other Conditions

The sample test sheets described above in general item 1 and treatment baths with the compositions reported in Table 1 were employed in a continuous treatment process in Examples 1 to 3 and Comparative Examples 1 to 4. For each example except

Comparison Examples 3 and 4, the upper row in each of the four rightmost columns of Table 1 and the six rightmost columns of Table 2 reports conditions prior to the continuous treatment process, while the lower row reports the level of these conditions after the continuous treatment process. In the case of Comparative Example 3 alone, the top row refers to conditions prior to the continuous process, the middle row refers to conditions after processing but prior to pH adjustment, and the bottom row refers to conditions after processing and after pH adjustment. (In Tables 1 and 2, "Ex" means "Example" and "C Ex" means "Comparative Example". In Table 2, "BTR" means "results of the accelerated testing of the resistance to black tarnishing" and "WRR" means "results of the accelerated testing of the resistance to white rust".)

Table 1

Identifier	Characteristics of the Treatment Composition									
	Concentration in g/L in the Composition of:									pH
	Fe	Co	Ni	PO ₄ ³⁻	F	Organic Acid	SO ₄ ²⁻	Zn	Al	
Ex 1	0	1.5	0	2.5	0.5	5.0 of ascorbic acid	39	25	0	3.1
							88	53	1.5	2.8
Ex 2	0.1	0	0	1.0	2.0	3.5 of glycolic acid	27	0	5.0	4.2
							72	27	5.8	3.9
Ex 3	2.0	0	1.0	0.7	1.5	2.0 of citric acid	18	5	1.0	2.2
							61	31	1.9	2.0
C Ex 1	0	1.5	0	2.5	0.5	5.0 of ascorbic acid	2	0	0	3.2
							47	25	1.3	3.0
C Ex 2	0	0	0	1.0	2.0	3.5 of citric acid	0	0	0	3.9
							6	3	0.2	1.9
C Ex 3	2.0	0	1.0	0	0	2.0 of citric acid	18	5	1.0	4.2
							40	21	0.8	5.3
							40	21	0.8	4.0
C Ex 4	No treatment (except subsequent chromating)									

Table 2

Identifier	Process Conditions				mg/m ² in Coating of:			BTR	WRR
	Contact by:	°C	Seconds of Contact	Sludge?	Fe	Co	Ni		
Ex 1	Spraying	50	5	No	0	2.4	0	+++	+++
				No	0	2.0	0	+++	+++
Ex 2	Immersion	60	10	No	0.2	0	0	+++	+++
				No	0	0	0	++	+++
Ex 3	Spraying	50	3	No	2.4	0	0.9	+++	++
				No	1.7	0	0.6	+++	+++
C Ex 1	Spraying	50	5	No	0	8.4	0	+++	×
				No	0	1.2	0	+++	+++
C Ex 2	Immersion	60	10	No	0	0	0	×	+++
				No	0	0	0	×	+++
C Ex 3	Spraying	50	3	No	1.3	0	0.2	++	+++
				Yes	0.1	0	0.1	×	++
				No	0.8	0	0.2	+	++
C Ex 4	No treatment (except subsequent chromating)							×	+++

The treated sample test sheets and untreated sample test sheet (Comparative Example 4) were then submitted to a dry-in-place chromate treatment as described in general item 2 above.

After treatment as described above, each of the sample test sheets was submitted to accelerated testing of the resistance to black tarnishing and white rusting as described in general items 3 and 4 above. Table 2 reports the following: the process conditions for the acidic treatment baths, the presence or absence of sludge production, the amount of heavy metal deposition after treatment, and the results of accelerated testing of the resistance to black tarnishing and white rusting.

The following conclusions can be drawn based on Examples 1 to 3, Comparative Examples 1 to 4, and Tables 1 and 2:

- In Examples 1 to 3, the amount of heavy metal deposition was restrained and an excellent resistance to black tarnishing and white rusting was obtained; no sludge was produced despite an increase in the amount of eluted ions; and the initial performance was maintained long-term.
- Comparative Example 1 lacked the initial presence of zinc ions and aluminum ions. In this case, the initial deposition of heavy metal was large and the resist-

ance to white rusting was poor.

- Comparative Example 2 lacked heavy metal ions. In this case, the etching reaction, which is the initial reaction in substitutional plating, is believed not to have occurred to any substantial extent in the short time employed, and the resistance to black tarnishing was poor.

- Comparative Example 3 lacked phosphoric acid and fluorine. In this case, a suitable degree of etching and a good resistance to black tarnishing were obtained with freshly made treatment solution. However, after continuous treatment and prior to pH adjustment, sludge was produced and the resistance to black tarnishing was poor. Even after the pH adjustment the resistance to black tarnishing was not improved, probably due to an inadequate etching.

- Comparative Example 4 did not employ the acidic treatment, and in this case the resistance to black tarnishing was poor.

Examples 4 to 6 and Comparative Examples 5 to 8 — General Conditions

The general conditions for these examples and comparative examples were the same as for Examples 1 to 3 and Comparative Examples 1 - 4, except as noted below:

1. The substrates were hot-dip coated with zinc-5 % aluminum alloy and were 0.5 mm thick.

2. A dry-in-place chromate bath (aqueous solution containing 2 % Cr(VI), 1 % Cr³⁺, and 5 % colloidal silica) was applied by roll coating so as to provide a chromium add-on of 30 mg/m². Application was followed by drying in a 200 °C convection drying oven to a maximum attained sheet temperature of 100 °C.

General items 3, 4, and 5 for this group were all the same as for Examples 1 to 3 and Comparative Examples 1 to 4.

Other Conditions

The sample test sheets described above in general item 1 and treatment baths with the compositions reported in Table 3 were employed in a continuous treatment process in Examples 4 to 6 and Comparative Examples 5 to 8. For each example except Comparative Example 8, the upper row in each of the four rightmost columns of Table 3 and the six rightmost columns of Table 4 reports conditions prior to the continuous treatment process, while the lower row reports the level of these conditions after the continuous treatment process. (Abbreviations in Tables 3 and 4 have the same meaning as in Tables 1 and 2.)

Table 3

Identifier	Characteristics of the Treatment Composition									
	Concentration in g/L in the Composition of:									pH
	Fe	Co	Ni	PO ₄ ³⁻	F	Organic Acid	SO ₄ ²⁻	Zn	Al	
Ex 4	0.5	0.5	0	1.0	2.0	1.2 of lactic acid	19	0	3.0	4.0
							85	25	8.0	3.5
Ex 5	1.0	0	0	2.5	1.0	3.0 of tartaric acid	10	5	0	2.5
							67	28	4.2	2.2
Ex 6	0	0	4.5	1.5	2.5	9.0 of malic acid	64	2	10.0	2.8
							130	30	14.5	2.1
C Ex 5	1.0	0	0	2.5	0	none	10	5	0	2.5
							69	39	1.3	1.0
C Ex 6	0	0	10.0	1.5	2.5	9.0 of malic acid	73	2	10.0	2.0
							204	53	19.8	1.5
C Ex 7	20 g/L of NaOH; ferric nitrate to contain 3 g/L of Fe; and NaAlO ₂ to contain 10 g/L of Al					15.0 of disodium salt of ethylenediamine tetraacetic acid	0	0	10.0	12.0
							0	2	6.1	12.0
C Ex 8	No treatment (except subsequent chromating)									

The treated sample test sheets and untreated sample test sheet (Comparative Example 8) were then submitted to a dry-in-place chromate treatment as described in general item 2 above.

- After treatment as described above, each of the sample test sheets was submitted to accelerated testing of the resistance to black tarnishing and white rusting as described in general items 3 and 4 above. Table 4 reports the following: the process conditions for the treatment baths, the presence or absence of sludge production, the amount of heavy metal deposition after treatment, and the results of accelerated testing of the resistance to black tarnishing and white rusting.

Table 4

Identifier	Process Conditions				mg/m ² in Coating of:			BTR	WRR
	Contact by:	°C	Seconds of Contact	Sludge?	Fe	Co	Ni		
Ex 4	Spraying	50	3	No	0.5	0.2	0	+++	+++
				No	0.3	0.1	0	+++	+++
Ex 5	Spraying	60	5	No	2.1	0	0	+++	+++
				No	1.9	0	0	+++	+++
Ex 6	Spraying	50	5	No	0	0	3.1	+++	+++
				No	0	0	1.8	+++	+++
C Ex 5	Spraying	60	5	No	4.5	0	0	+++	++
				No	0.4	0	0	+	+++
C Ex 6	Spraying	50	5	No	0	0	7.5	+++	×
				No	0	0	0.4	++	+
C Ex 7	Spraying	50	3	No	2.5	0	0	+++	+++
				Yes	0.1	0	0	+	+++
C Ex 8	No treatment (except subsequent chromating)							×	+++

The following conclusions can be drawn based on Examples 4 to 6, Comparative Examples 5 to 8, and Tables 3 and 4:

- In Examples 4 to 6, the amount of heavy metal deposition was restrained and an excellent resistance to black tarnishing and white rusting was obtained; no sludge was produced despite an increase in the amount of eluted ions; and the initial performance was maintained long-term.
- Comparative Example 5 lacked the presence of fluoride ions and organic acid. The absence of the organic acid resulted in a low pH-buffering capacity during the continuous treatment, and the pH therefore suffered from an excessive decline due to the large amount of sulfuric acid replenishment. The resulting concern with regard to equipment corrosion led to cessation of the treatment process. In addition, the low pH notwithstanding, even prior to cessation Comparative Example 5 gave an inadequate etching, due to the absence of the fluoride ions, which resulted in a poor resistance to black tarnishing.
- Comparative Example 6 used a large amount of heavy metal ions. This resulted in a poor resistance to white rusting during initial operations due to the inability to restrain the amount of heavy metal ions deposition. In the ensuing continuous

operations, large amounts of sulfate ions were required to scavenge the zinc and aluminum ions as a consequence of the strong etch. This resulted in residual sulfate ions on the surface of the test sheet, which led to a poor resistance to white rusting.

- 5 - Comparative Example 7 used an alkaline instead of an acid treatment. In this case large amounts of sludge were produced by the continuous process. The associated coprecipitation of the heavy metal ions led to an inadequate etch and therefore to a reduced resistance to black tarnishing.
- 10 - Comparative Example 8 did not employ any treatment before chromating, and in this case the resistance to black tarnishing was poor.

BENEFITS OF THE INVENTION

At least in its preferred embodiments, the present invention: provides an improved resistance to black tarnishing and an improved resistance to white rust; makes possible continuous use of its acidic aqueous solution with long-term retention of the initial performance of the solution; and is almost entirely free of equipment corrosion.

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CLAIMS

1. A process for treating a surface of a metal substrate to reduce the corrosion and discoloration that the surface will suffer after such treatment, said process comprising operations of:
- 5 (I) contacting a metallic surface with an acidic aqueous treatment solution having a pH from 1.5 to 4.5 and comprising water and:
- (A) at least one type of heavy metal cations selected from the group consisting of iron, cobalt, and nickel; and
- (B) zinc ions, aluminum ions, or both aluminum and zinc ions;
- 10 (II) discontinuing the contacting of operation (I) and thereafter rinsing said metallic surface with water; and
- (III) discontinuing the rinsing of operation (II) and thereafter coating said metallic surface with a liquid layer of an aqueous chromating solution comprising water and hexavalent chromium; and
- 15 (IV) without any rinsing after operation (III), drying into place on said metallic surface the liquid layer formed in operation (III).
2. A process according to claim 2, wherein said acidic aqueous solution comprises the following components:
- (A) a total of from 0.05 to 5 g/L of heavy metal cations;
- 20 (B) a total of from 1 to 50 g/L of zinc ions, aluminum ions, or both aluminum and zinc ions;
- (C) from 1 to 200 g/L of sulfate ions;
- (D) from 0.3 to 3 g/L of phosphate ions;
- (E) from 0.3 to 3 g/L of fluoride ions; and
- 25 (F) a total of from 1 to 15 g/L of at least one organic acid selected from the group consisting of glycolic acid, lactic acid, malic acid, tartaric acid, citric acid, gluconic acid, and ascorbic acid.
3. A process according to claim 2, wherein, in said acidic aqueous solution before it has begun to be used for treatment:
- 30 - the concentration of component (A) is from 0.1 to 1.5 g/L;
- the concentration of component (B) is from 3.0 to 35 g/L;
- the concentration of component (C) is from 10 to 65 g/L;
- the concentration of component (D) is from 0.7 to 2.5 g/L; and
- the concentration of component (E) is from 0.5 to 2.5 g/L.
- 35 4. A process according to claim 3, wherein, as the process continues with treatment

of more metallic substrate surface, additional sulfuric acid is added to the acidic aqueous treatment solution in an amount such that the pH value of the treatment solution does not rise by more than 0.50 pH unit above nor fall by more than 1.1 pH unit below its pH value before it began to be used in the process.

5 5. A process according to claim 4, wherein the pH value of the treatment solution does not rise by more than 0.10 pH unit above nor fall by more than 0.7 pH unit below its pH value before it began to be used in the process.

6. A process according to claim 5, wherein:

- 10 - during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 18 to 80 °C;
- contacting during operation (I) is for not more than 15 seconds;
- the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 5 mg/m²;
- operation (II) utilizes a sufficient volume of rinse water that any of the acidic aqueous treatment solution that remains on the surface of the metal substrate
15 after operation (I) is diluted at least 500-fold; and
- during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 50 to 100 °C.

7. A process according to claim 6, wherein:

- 20 - during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 47 to 63 °C;
- contacting during operation (I) is for from 2.5 to 10 seconds;
- the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 3.5 mg/m²; and
- 25 - during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 60 to 100 °C.

8. A process according to claim 1 wherein, as the process continues with treatment of more metallic substrate surface, additional sulfuric acid is added to the acidic aqueous treatment solution in an amount such that the pH value of the treatment solution does
30 not rise by more than 0.50 pH unit above nor fall by more than 1.1 pH unit below its pH value before it began to be used in the process.

9. A process according to claim 8, wherein the pH value of the treatment solution does not rise by more than 0.10 pH unit above nor fall by more than 0.7 pH unit below its pH value before it began to be used in the process.

10. A process according to claim 9, wherein:
- during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 18 to 80 °C;
 - contacting during operation (I) is for not more than 15 seconds;
 - 5 - the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 5 mg/m²;
 - operation (II) utilizes a sufficient volume of rinse water that any of the acidic aqueous treatment solution that remains on the surface of the metal substrate after operation (I) is diluted at least 500-fold; and
 - 10 - during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 50 to 100 °C.
11. A process according to claim 10, wherein:
- during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 47 to 63 °C;
 - 15 - contacting during operation (I) is for from 2.5 to 10 seconds;
 - the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 3.5 mg/m²; and
 - during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 60 to 100 °C.
- 20 12. A process according to claim 1 wherein, as the process continues with treatment of more metallic substrate surface, additional sulfuric acid is added to the acidic aqueous treatment solution in an amount such that the pH value of the treatment solution does not rise by more than 0.50 pH unit above nor fall by more than 1.1 pH unit below its pH value before it began to be used in the process.
- 25 13. A process according to claim 12, wherein the pH value of the treatment solution does not rise by more than 0.10 pH unit above nor fall by more than 0.7 pH unit below its pH value before it began to be used in the process.
14. A process according to claim 13, wherein:
- during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 18 to 80 °C;
 - 30 - contacting during operation (I) is for not more than 15 seconds;
 - the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 5 mg/m²;
 - operation (II) utilizes a sufficient volume of rinse water that any of the acidic

- aqueous treatment solution that remains on the surface of the metal substrate after operation (I) is diluted at least 500-fold; and
- during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 50 to 100 °C.
- 5 15. A process according to claim 14, wherein:
- during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 47 to 63 °C;
 - contacting during operation (I) is for from 2.5 to 10 seconds;
 - the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 3.5 mg/m²; and
 - 10 - during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 60 to 100 °C.
16. A process according to claim 1, wherein:
- during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 18 to 80 °C;
 - 15 - contacting during operation (I) is for not more than 15 seconds;
 - the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 5 mg/m²;
 - operation (II) utilizes a sufficient volume of rinse water that any of the acidic aqueous treatment solution that remains on the surface of the metal substrate after operation (I) is diluted at least 500-fold; and
 - 20 - during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 50 to 100 °C.
17. A process according to claim 16, wherein:
- 25 - during operation (I), the acidic aqueous solution is maintained at a temperature in a range from 47 to 63 °C;
 - contacting during operation (I) is for from 2.5 to 10 seconds;
 - the amount of heavy metal deposited on the treated metal substrate in operation (I) is less than 3.5 mg/m²; and
 - 30 - during operation (IV), the maximum temperature reached by the metallic substrate is within a range from 60 to 100 °C.
18. A process according to any one of claims 1 through 17, wherein the metallic substrate surface treated contains at least 50 % of zinc.
19. A process according to claim 18, wherein the metallic surface treated has been

formed by hot-dip galvanizing of steel.

20. An acidic liquid composition of matter useful as a treatment liquid in operation (I) of a process according to claim 2, said acidic aqueous liquid comprising water and the following components:

- 5 (A) a total of from 0.05 to 5 g/L of heavy metal cations;
 - (B) a total of from 1 to 50 g/L of zinc ions, aluminum ions, or both aluminum and zinc ions;
 - (C) from 1 to 200 g/L of sulfate ions;
 - (D) from 0.3 to 3 g/L of phosphate ions;
 - 10 (E) from 0.3 to 3 g/L of fluoride ions; and
 - (F) a total of from 1 to 15 g/L of at least one organic acid selected from the group consisting of glycolic acid, lactic acid, malic acid, tartaric acid, citric acid, gluconic acid, and ascorbic acid.
21. A composition according to claim 20, wherein:
- 15 - the concentration of component (A) is from 0.1 to 1.5 g/L;
 - the concentration of component (B) is from 3.0 to 35 g/L;
 - the concentration of component (C) is from 10 to 65 g/L;
 - the concentration of component (D) is from 0.7 to 2.5 g/L; and
 - the concentration of component (E) is from 0.5 to 2.5 g/L.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/00042

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 28/00, 22/82, 22/07

US CL : 148/255, 256, 259, 261, 262

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/255, 256, 259, 261, 262

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS search terms: zinc phosphate, zinc, nickel, aluminum, sulfate, organic acid, chelating agent, chromium, fluoride, surface, metal, phosphate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,624,480 A (YOSHITAKE et al) 29 April 1997, col. 9, table 3; claim 1; col. 6, lines 35 to col. 7, line 55; col. 5, lines 9-11; col. 3, line 44; col. 1, lines 21-24.	1-3, 18, 20-21 --- 4-17, 19
Y	GB 1,415,999 A (PYRENE CHEMICAL SERVICES LIMITED) 03 December 1975, page 2, lines 79-91; page 2, lines 50-75; claim 1.	1-21
Y	US 3,664,887 A (ATKISS) 23 May 1972, col. 2, lines 12-15; claim 1.	1-21
A	US 2,132,000 A (CURTIN et al) 07 October 1936, col. 1, lines 19-23; col. 2, lines 15-17; claim 1.	1-21
A	US 4,153,479 A (AYANO et al) 08 May 1979, col. 2, lines 12-27; examples 2-6; claim 1.	1-21

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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P document published prior to the international filing date but later than the priority date claimed		

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